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Recycling Isotopically Enriched Mo from the RadioGenix Waste Stream

Chemical & Fuel Cycle Technologies Division

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ABSTRACT

NorthStar's RadioGenix generator utilizes an aqueous biphasic extraction chromatography column to separate Tc from low-specific-activity ^{99}Mo. During this separation process, a fraction of the source Mo material can be found in the waste. This is not of concern when natural Mo targets are used. However, the introduction of isotopically enriched ^{98}Mo for neutron capture or ^{100}Mo for accelerator-based production requires recovery of this valuable enriched Mo material. The generator waste is absorbed and solidified in a superabsorbent hydrogel polymer. In this contribution, we report results from our small-scale experimental study on development of a separation process for recovery of molybdenum from the polymeric gel waste using common chemicals and simple chemical techniques.

Our investigation confirms that the acidic deswelling of the alkaline hydrogel with concentrated hydrochloric acid converts the occluded molybdate to a neutral molybdenyl dichloride species that is freely released from the gel. Mo can then be concentrated on a commercial tri-*n*-butyl phosphate resin, eluted with ammonium hydroxide, and crystallized as ammonium heptamolybdate for conversion back to Mo metal. Typical Mo recoveries are 90–95%.

1 INTRODUCTION

The development and implementation of alternative technologies to produce ^{99}Mo/^{99m}Tc without the use of ^{235}U has recently attracted a lot of interest; these technologies include i) ^{100}Mo(γ,n)^{99}Mo via photonuclear reaction with a photon source from bremsstrahlung, ii) ^{100}Mo(n,2n)^{99}Mo using fast neutrons, and iii) neutron capture on ^{98}Mo. These approaches offer a less-expensive alternative to fission-made ^{99}Mo, but with a lower yield. The main advantage of these alternative technologies is the minimal amount of low-level waste generated, owing to minimal purification requirements. However, to produce several kCi of ^{99}Mo, enriched ^{98}Mo or ^{100}Mo targets are required (enriched ^{100}Mo is available in kg quantities for ~ $1000/g). One of the difficulties with production of low specific-activity ^{99}Mo/high-specific-activity ^{99m}Tc is the need for a different generator designed to accommodate the low specific activity of ^{99}Mo.

NorthStar's RadioGenix® generator is designed for separation of ^{99m}Tc from low-specific-activity ^{99}Mo in highly alkaline solution. It uses a Tc-selective aqueous biphasic extraction chromatography (ABEC) resin in a multicolumn design (Figure 1). Small amounts of Mo that pass through the ABEC column can partition to the waste stream, where the solution is absorbed and solidified in a superabsorbent polymer. This is not a problem when natural Mo targets are used, but the high cost of enriched Mo material (^{100}Mo or ^{98}Mo) requires that the Mo in the waste stream be efficiently recycled into fresh targets.

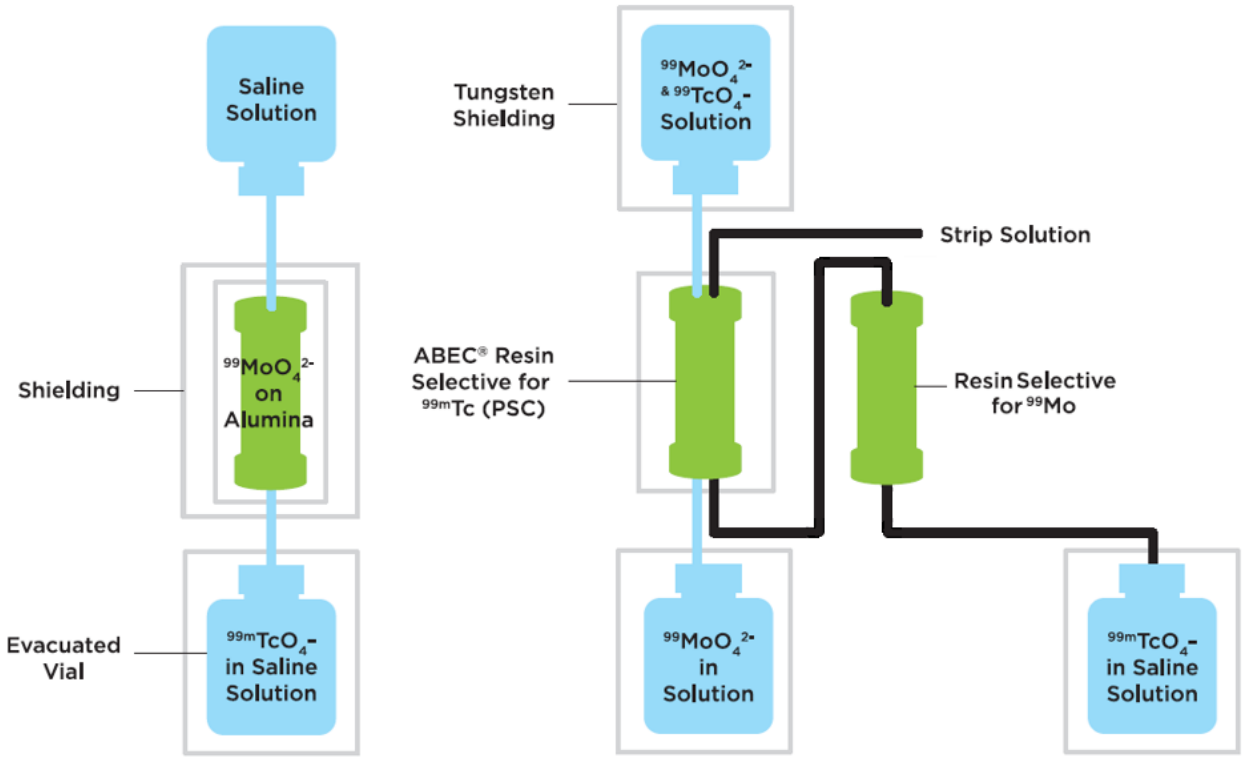

FIGURE 1 Comparison of traditional ion-exchange column (left) and a generic multicolumn selectivity inversion generator on which the RadioGenix system is based (right); adapted from Horwitz and Bond [1].

The RadioGenix generator uses a modified superabsorbent polymer, Northstar Blue (NSB) to capture its waste stream. The waste stream is highly alkaline, comprising primarily aqueous NaOH solution. Fresh containers with 350 g of dry NSB polymer collect up to 3.5 L of used Mo solution (~200 elutions), at which point the containers are replaced. The final waste matrix contains around 10 mL of waste solution per gram of dry polymer. Each waste containiner may hold up to several grams of Mo.

The composition of NSB is a proprietary mixture of two hydrogel copolymers consisting of crosslinked poly(acrylamide-co-acrylic acid). An example of the poly(acrylamide-co-acrylic acid) structure is depicted in Figure 2 [2]. These commercially available polymers are commonly used for their superabsorbent qualities and ability to sequester harmful multivalent cations. The ratio of comonomers is often tuned to achieve the desired gel properties. In general, the non-ionic acrylamide monomers add mechanical strength, allowing the hydrogel beads to retain their spherical shape. Acrylate monomers participate in hydrogen bonding and enhance the absorption capacity for liquid solutions. The molecular weights of the polymer and its crosslinkers allow for additional tunability of its features. Longer (high-molecular-weight) crosslinkers between chains allow for greater swellability compared to shorter (low-molecular-weight) crosslinkers.

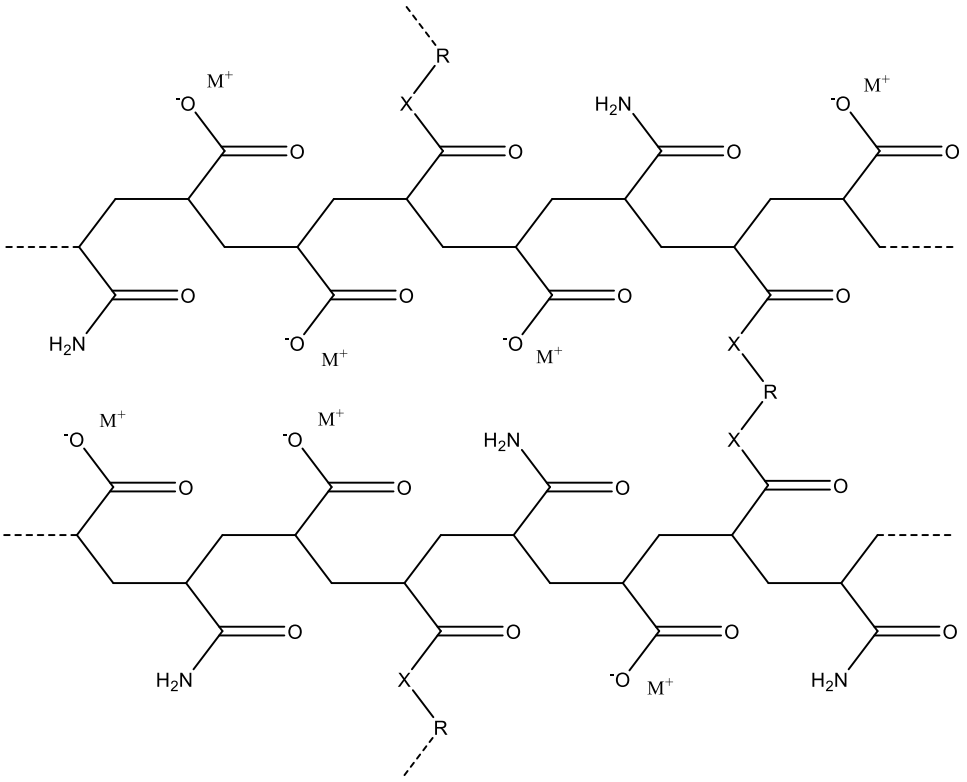

FIGURE 2 Poly(acrylamide-co-acrylic acid) polymer network. M+ = Na+, R = CH_2, and X = NH or O. Adapted from Zohuriaan-Mehr and Kabiri [2].

Poly(acrylamide-co-acrylic acid) is an atactic, weakly anionic polyelectrolyte containing ionizable groups that are able to dissociate in aqeuous media [3]. The dissociation of positive counterions in solution creates a high charge density along its backbone, which allows repulsive forces between charged groups to extend the polymer chain. Water capture is facilitated by hydrogen bonding within the three-dimensional framework of crosslinked chains. As a result, anionic hydrogels are able to absorb 100 to 1000 times their mass of neutral- to high-pH aqueous solutions.

Hydrogen bonding in hydrogels can be disrupted by the neutralization of the charged groups. In anionic hydrogels, high-ionic-strength and high-acid conditions greatly reduce the absorption capacity for water. Decreasing the pH environment of a fully swollen anionic hydrogel can result in the collapse, or deswelling, of the gel and release of absorbed solution [2]. It is important to consider the deswelling behavior when recovering absorbed Mo solutions, which are highly alkaline.

A poly(acrylamide-co-acrylic acid) chain is typically synthesized by solution or suspension polymerization using the desired ratio of monomeric subunits in a mixture. However, the copolymer can also be derived from homogeneous polyacrylamide following the partial hydrolysis of amide moieties [4]. Amide groups will hydrlyze to carboxyl groups under both alkaline and acidic conditions through, for example, the reactions [5]

$$CH_3CONH_2 + NaOH \rightarrow CH_3COONa + NH_3 \quad (1)$$

$$CH_3CONH_2 + H_2O + HCl \rightarrow CH_3COOH + NH_4^+Cl^- \quad (2)$$

The result of amide hydrolysis of polyacrylamide is the partial or complete conversion to polyacrylate and release of ammonia. Partial degradation of the NSB polymer is apparent in RadioGenix waste (pH ~14), which offgasses ammonia.

The high charge density in anionic hydrogels enables the binding and sequestration of various multivalent cations (e.g., Ca^{2+}, Co^{2+}, Al^{3+}, MoO_2^{2+}) following the dissociation of positive counterions (Na^+, K^+) [6]. Polymers with carboxyl groups ($-COO^-$) can precipitate as M^{2+}-polyacrylates (eg. M = Ca, Mg, Ba) [7] [8]. Precipitation is due to metal-bridged complexing that takes place between two neighboring monomers along an individual chain, causing the polymer backbone to shrink. This effect is known as counterion condensation or "salting out," and results in flocculation of metal-polymer aggregates. Flocculation of dissolved metals makes polyacrylate useful for wastewater treament [5].

Hydrogels that precipitate through complexation with multivalent cations show limited resolubilization in aqueous solutions. This feature may be leveraged for phase separation in NSB. Divalent counterions show strong affinity for polyacrylates in saline solutions and have been generally classified in the order [3] $Mg^{2+} < Ca^{2+} < Ba^{2+} < Mn^{2+} < Co^{2+} < Ni^{2+} < Cd^{2+} << Cu^{2+}$. However, dissolved metals typically show reduced binding to polyacrylate in matrices of high acidity and ionic strength [9]. One exception to this rule is metals that form complexes in acidic solutions. The molybdenyl oxocation MoO_2^{2+} that forms at pH < 0 may therefore coprecipitate with polyacrylate [10]. The use of a complexing acid such as HCl can preclude the formation of MoO_2^{2+}, favoring the chloro-complex MoO_2Cl_2.

The extraction of Mo from the polymer will still require purification steps to remove Na and K before Mo is recycled to ammonium heptamolybdate (AHM). One method available to accomplish this purification leverages the extractability of MoO_2Cl_2 in HCl using the neutral extracting ligand tri-n-butyl phosphate (TBP) [11]. Our group has previously optimized this process in the recycling of source Mo targets (MOEX process), which achieves quantitative Mo recoveries and excellent Na and K decontamination [12]. The MOEX process was recently implemented in large-scale, rapid processing schemes using countercurrent centrifugal contactors [13]. Mo is recovered in ammonium hydroxide, which is evaporated to form solid AHM. The AHM powder is heated in a furnace, where it is converted to Mo metal. An investigation into the continous recycling of K_2MoO_4 source material is ongoing and is presented in a separate report.

Typical RadioGenix waste containers may contain up to several-gram quantities of enriched Mo metal. It is important to recycle this Mo back to AHM for the production of new targets for irradiation. The purpose of this study is to provide an efficient method for the recovery of enriched Mo from the NSB gel waste. Preliminary data on solvent extraction and column chromatographic separation of Mo recovered from NSB are also presented.

2 EXPERIMENTAL

2.1 REAGENTS

All chemicals were purchased from Fisher Scientific and used as received. Hydrochloric acid was trace-metal grade, and all water was deionized and purified to >18 MΩ-cm. When impurities were being measured, glassware was acid-washed thoroughly prior to use. Simulated RadioGenix waste solutions were prepared according to a proprietary composition provided by NorthStar, consisting of NaOH, KOH, NaCl, and Mo^{6+} at pH 14.3. The pH of all solutions was determined by titration with phenolphthalein using standardized NaOH or HCl.

NSB polymer was received from NorthStar i) in dry polymer form and ii) as a gel containing actual RadioGenix waste solution. When preparing NSB gel simulant from dry NSB polymer, simulant solution was added using a ratio of 10 mL/1 g polymer and allowed to equilibrate for 12–24 hours. The mixture underwent a color change from blue to pink during the equilibration period, with a final pH around 14. Metal concentrations were determined by inductively coupled plasma mass spectrometry (ICP-MS).

2.2 POLYMER DESWELLING

Small-scale experiments were performed using either a glass fritted vacuum filtration apparatus (Figure 3) with a glass-wool prefilter with 2-µm pore size, or Milllipore low-binding Durapore PVDF membrane centrifuge tubes with 0.22-µm pore size. NSB gel was added to sample containers by mass; then deswelling solutions were added at an approximately 1:1 volume ratio. The mixture was stirred or vortexed thoroughly and allowed to settle for at least one hour to allow equlibration, during which time no further changes to the mixture were apparent. Samples were then filtered or centrifuged for 5 min at 2500 rpm to separate liquid and solid phases.

Reactions on a larger scale were performed in open glass beakers with overhead stirring to allow offgassing of ammonium chloride. The solid phase settled to the bottom of the container and tackified together, forming a cake. This mixture was filtered over a medium glass frit under full vacuum. The solid phase was then immediately washed or soaked in HCl solution to recover the remaining Mo. Liquid phases that were turbid after filtration were filtered again, using a 0.45-µm PVDF filter. The ingrowth of various impurities was determined by ICP-MS and compared to a system blank of trace-metal-grade HCl, which was collected through the same filtration apparatus. Temperature measurements were recorded using a Teflon-coated k-type thermocouple.

FIGURE 3 Filtration apparatus for separating NSB polymer from the liquid effluent.

Polymer deswelling was quantified in terms of the deswelling ratio (DR) shown in Eq. 3, where m_s is the weight of the swollen polymer and m_d is the weight of the final dry state [14]:

$$DR(\%) = 100\ x\ \frac{m_s - m_d}{m_s} \quad (3)$$

Mo recoveries were measured using ^{99}Mo radiotracer obtained from a commercial ^{99}Mo/^{99m}Tc generator (Lantheus Medical Imaging). Solid and liquid phases were transferred to 20-mL liquid scintillation vials prior to counting. Gamma counting of ^{99}Mo was performed on either an HPGe detector (Ortec) or a NaI gamma counter (Perkin Elmer), using the 740-keV peak.

2.3 PURIFICATION OF RECOVERED Mo

Solvent extraction experiments were performed using the effluent recovered from NSB gel acidified to 5M HCl. This solution was added to an organic phase of 30% (v/v) TBP in tetrachloroethylene (TCE). The mixture was vortexed continuously for 20 min and centrifuged at 2000 rpm for 5 min. The organic phase was stripped using 3M $NH_{3(aq)}$, mixed for 5 min, and centrifuged. All aquous-phase volumes were recorded and Mo concentrations were determined by ICP-MS.

Chromatography experiments were done using commercial TBP resin (Triskem Inc.) with 50- to 100-µm particle size. Resin was dry packed into columns with 10-mm inner diameter and 20-µm-porosity polyethylene frits. The packed resin was pre-conditioned with 3 bed volumes of 5M HCl for at least 12 hours to ensure proper wetting. Gravity flow rates (approximately 1–2 mL/min) were used. Aliquots of the eluates were collected in 4-mL polypropylene gamma-counting tubes or 20-mL liquid scintillation vials and counted as previously described.

3 RESULTS AND DISCUSSION

3.1 DESWELLING EXPERIMENTS

The plot in Figure 4 summarizes the key findings from deswelling experiments. The characteristics of NSB gel were investigated by adding HCl or brine solutions of monovalent (Na^+) or divalent (Ca^{2+}) cations. The purpose of these experiments was to determine conditions under which the maximum volume of Mo solution was desorbed from the gel and how they relate to Mo recovery. A second important consideration was the solid-phase characteristics after precipitation. In each case, the supernatant phase contained organic material leached from NSB, which was evident from the effluent color and the turbidity of the solution. Therefore, purification of the effluent to remove dissolved organics was required regardless of the added solution.

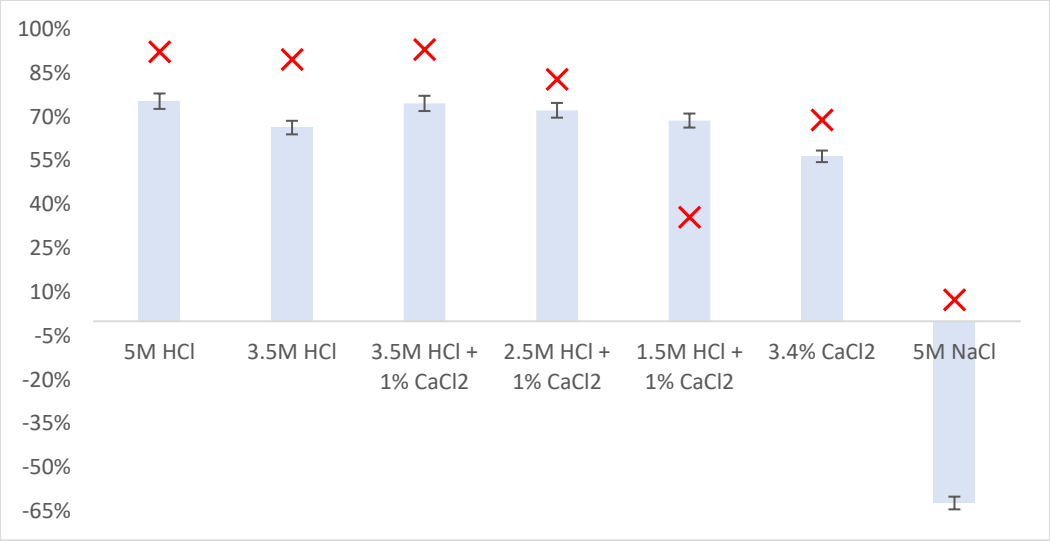

FIGURE 4 Deswelling of NSB hydrogel (columns) and Mo recovery (red X symbols) using HCl and $CaCl_2$. Concentrations correspond to the composition of solutions added to NSB gel (1:1 v/v).

In general, gel treated with HCl decreased in mass and settled to the bottom of the sample vial, where it formed a tackified precipitate. The polymer collapses because of neutralization of charges along the polymer chain by protonation or cation exchange with Ca^{2+}. Precipitation reactions appeared to reach equilibrium within 15 min, after which the mass of the precipitate remained constant. Gels treated with HCl concentrations of 5M or greater were similar to each other in their solid-phase characteristics. At concentrations lower than 5M HCl, the gel did not fully deswell and remained adherent to container surfaces. Gel treated with $CaCl_2$ brine formed a dense, white solid phase, indicating the precipitation of Ca-polyacrylate. As expected, the NaCl brine was mostly absorbed by the polymer, resulting in an overall increase in gel mass. The absorption of NaCl brine shows that RadioGenix waste gel is below its swelling capacity for high-ionic-strength solutions.

Ca^{2+} and HCl were both effective at deswelling the hydrogel and releasing the Mo to the liquid phase. Maximum Mo recoveries (93%) and gel deswelling ratios (75%) were obtained from samples treated with ≥3.5M HCl, irrespective of $CaCl_2$ content. Below the maximum deswelling ratio, adding 1% $CaCl_2$ to HCl resulted in improved deswelling compared to $CaCl_2$-free solutions, but not improved Mo recovery.

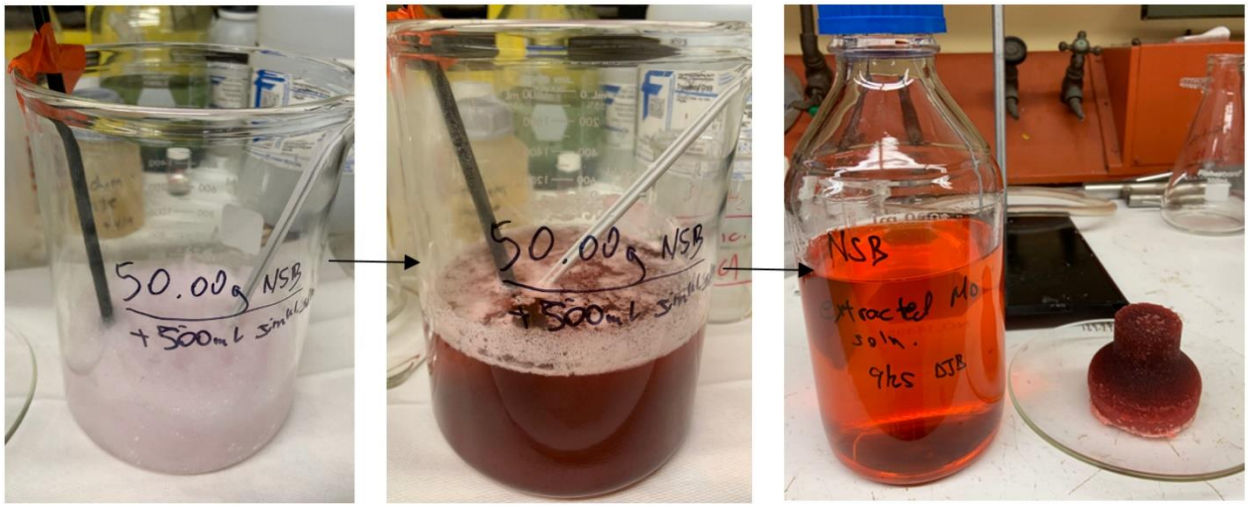

FIGURE 5 RadioGenix-simulated NSB gel (left), gel treated with HCl (middle), and the resulting liquid and solid phases after filtration (right).

While the addition of $CaCl_2$ did not improve Mo recovery in HCl solutions, its effect on the precipitate characteristics may be useful in the larger-scale processing of NSB. Ca precipitation produced denser and less adherent gel precipitates. This characteristic could help to simplify waste handling and reduce surface contamination on laboratory equipment. In addition, $CaCl_2$ may be used to remove organic material that is leached to the aqueous stream during deswelling. This idea follows a similar principle used in wastewater treatment processes, where polyacrylates are used to remove metal contaminants by flocculation. However, adding $CaCl_2$ could produce undesired downstream effects, which were not investigated in this study. For example, Ca^{2+} may partition into the Mo fraction and affect the purification of Mo. $CaCl_2$ was therefore excluded from further experiments.

3.2 Mo RECOVERY WITH HCl

Mo recovery as a function of HCl concentration (0.5-10M) was further explored without added $CaCl_2$. The data in Figure 6 show that more than 90% of Mo can be extracted from the polymer using HCl concentrations of 3M or greater; above 3M HCl, the differences are minimal. The liquid matrix obtained is similar to that used in MOEX processing (≥5M HCl) [12]. Therefore, strong HCl solutions were used for all remaining experiments. The final acidity of NSB gel when treated with 11M HCl is around 5M H^+, as determined by titration.

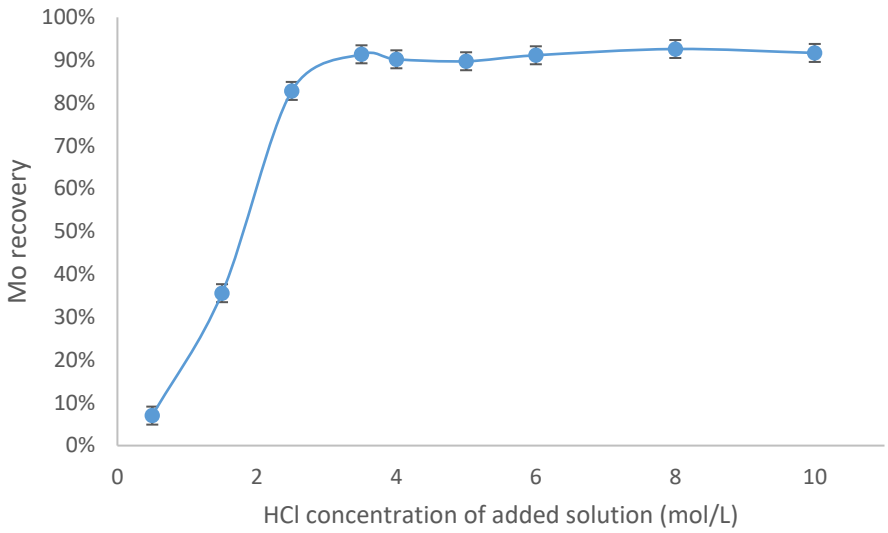

FIGURE 6 Total Mo recovery from NSB gel versus HCl concentration, after 1-hour equilibration time at room temperature. The HCl concentration represents the solution added to the gel, since the resulting mixture is a complex matrix.

Washes of the gel were measured to determine the Mo recoveries per wash volume. Data in Table 1 show that the majority of Mo is carried in the effluent during the first filtration. Mo recovery (75%) is consistent with the gel deswelling ratios under these conditions (75%), indicating that Mo was solvated by HCl and minimally associated with the precipitated polymer. Consecutive HCl washes were able to remove most of the remaining Mo. The solid phase contained the remaining Mo (7%).

TABLE 1 Mo recovery from NSB gel treated with 10M HCl. A 5-g sample of ^{99}Mo-spiked NSB simulant gel was deswelled with 5 mL of HCl for a 1-hour equilibration time prior to vacuum filtration.

	Mo
Effluent	74.9%
Wash 1 – 2 mL, 5M HCl	11.4%
Wash 2 – 2 mL, 5M HCl	5.4%
Wash 3 – 2 mL, 5M HCl	1.5%
Total Mo recovered	**93.2%**

Figure 7 shows the kinetics of Mo extraction from the gel after acidification with 11M HCl in a 1:1 volume ratio. The data show that the bulk of the Mo extraction occurred very rapidly, with 89% of the Mo in the liquid phase after the first 2 min of contact time. This recovery rate parallels the rate of gel precipitation from deswelling experiments. However, when solid phases were then soaked in 5M HCl for an additional 12 hours, near-quantitative Mo recoveries were obtained.

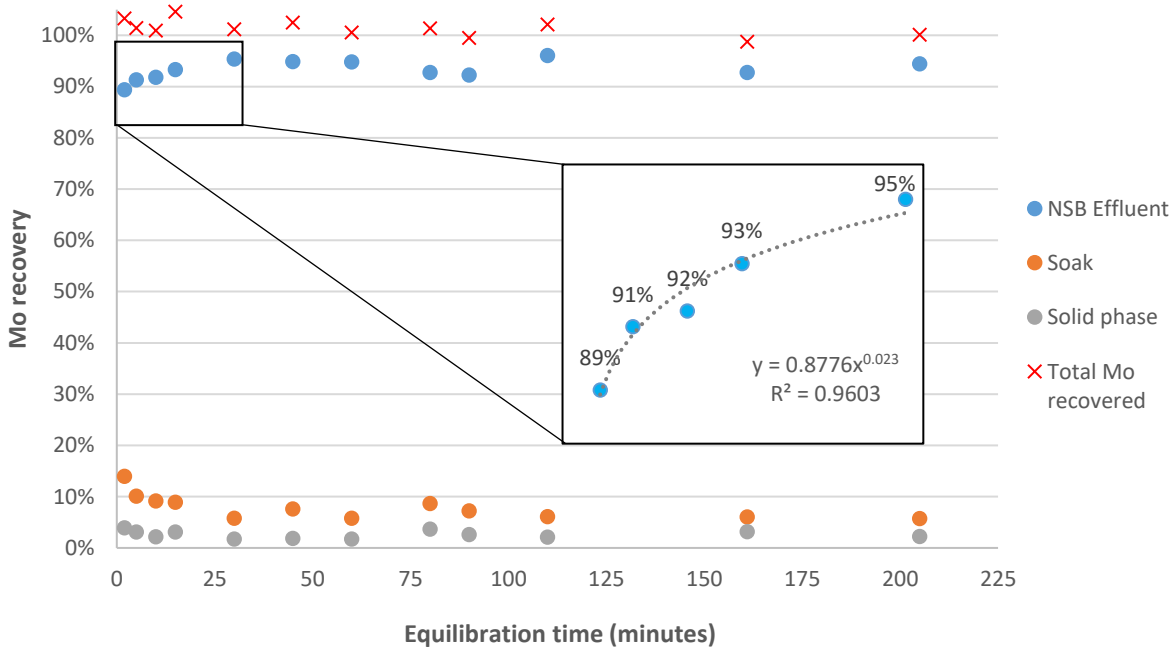

FIGURE 7 Mo recovery from NSB using concentrated HCl with different equilibration times. The mixture was vortexed intermittently, then filtered and washed at the corresponding time point. Each solid phase was then subjected to a 12-h soak in 5M HCl to recover the remaining Mo.

Extraction equilibrium was reached within 30 min of contact time with HCl. The slow equilibration time is most likely caused by the diffusion-limited exchange of Mo through the dense polymer, which rapidly shrinks during the first 2 min of contact with HCl. Extended equilibration times in concentrated HCl caused signs of acidic degradation of the polymer after several days. It is possible that very high HCl concentrations cause the scission of the CH_2-CHR-CH_2 backbone and dissolution of low-molecular-weight fragments [15]. It is important to minimize the degradation of the polymer, which would complicate downstream purification processes. Therefore, soaking was done in 5M HCl, which produced no apparent signs of polymer degradation by 72 hours.

Table 2 shows the average values for Mo recovered after the mixture reached equilibrium (in ≥ 30 min). It can be seen that the majority of Mo is released from the polymer during the first HCl contact. Roughly 6–12% of Mo is left in the solid phase after the first HCl contact. Soaking

the solid phase in 5M HCl led to extraction of most of the remaining Mo and reduced Mo losses to around 2%.

TABLE 2 Average equilibrium values for Mo recovery at each stage.

	Mo Recovery ± S.D.
Effluent + washes	94.1% ± 1.3%
5M HCl soak	6.6% ± 2.4%
Solid phase	2.4% ± 0.7%
Total recovery	**100.7% ± 1.2%**

Overall, the data suggest that Mo can be nearly quantitatively separated from the bulk of the organic polymer using strong HCl. Two contacts of the gel with strong HCl, one 11M-HCl deswelling period and one 5M-HCl soak, were able to recover 98–100% of the Mo. However, as previously mentioned, the effluent from this reaction contains small amounts of organic contaminants derived from the NSB polymer. This is evident from the effluent color and occasional turbidity of recovered solutions. Mo must be separated from organic material prior to target fabrication. Preliminary experiments on the removal of organic contaminants will be discussed in later sections of this report.

3.3 SCALED-UP PROCESSING OF NSB

A large 600-g batch of simulated RadioGenix waste was acidified with 11M HCl to test the scaled-up process. Solution volumes and other reaction characteristics were recorded. Results from these experiments are shown in Table 3 and Figure 8.

TABLE 3 Volumes and deswelling ratio (DR) from a 600-g waste batch treated with HCl.

	Mass (g)	Volume (L)
Initial NSB polymer	50.00	-
Simulant solution	548	0.50
Total starting gel	598	
11M HCl	-	0.55
5M HCl washes	-	0.04
Total volume of starting solution	-	1.09
Recovered liquid phase	-	1.00
Recovered solid phase	126.5	-
DR (%)	79%	

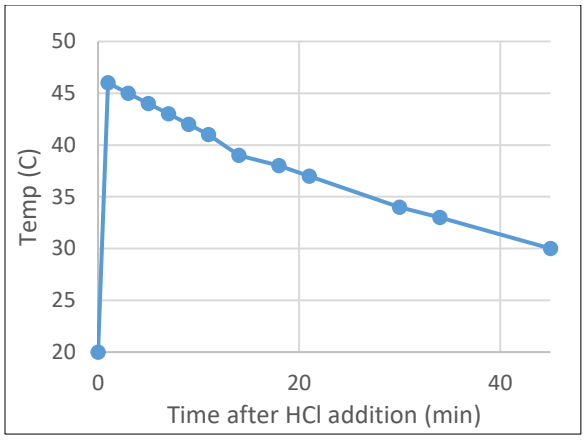

FIGURE 8 Solution temperature recorded during deswelling of 600-g NSB gel with concentrated HCl.

It was noticed during large-scale processing of NSB gel that adding HCl resulted in the release of heat and white vapor, and foam formation. The recorded temperature reached a maximum of 47°C. It is likely that heat release is mainly due to the exothermic reaction of acid-base neutralization. Vapor formation is the result of acidic degradation of amide groups of the polymer, generating a carboxylic acid group and free ammonium ion. Liberated gaseous ammonia reacts with HCl fumes to produce white ammonium chloride gas following the reaction

$$NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(g)} \quad (4)$$

Hydrolysis of amide groups likely occurs on the acrylamide monomers but may also occur on crosslinkers between chains, resulting in the de-crosslinking and release of water-soluble polyacrylate fragments. However, the solid phase appeared to remain undissolved as a tackified precipitate. The overall reduction in NSB gel mass was 79%. The gel precipitate can be air-dried over several days to further reduce its mass, resulting in a low-activity, compact waste form.

3.4 IMPURITIES

The purity of the extracted Mo product will be affected by contaminants accumulated from the RadioGenix system or from NSB. The tabulated results from the ICP-MS analysis of simulated and NSB-derived waste are displayed in Table 4. Data from these samples were compared with a system blank using trace-metal-grade HCl filtered through the same apparatus.

TABLE 4 Impurities detected by ICP-MS after treatment of NSB waste gel (simulated and NSB-derived) with concentrated HCl. Error associated with ICP-MS detection is ±10%.

	Conc. (ppm)		
Element	Simulated Waste Solution	Effluent from Simulated Waste Gel (60-g Sample)	Effluent from RadioGenix Waste Gel (55-g Sample)
Mo	3370	1400	1030
Na	55100	35200	34700
K	3910	1690	2120
P	ND[a]	4.48	9.13
Zn	ND	0.73	0.20
Sn	ND	0.18	0.19
Cu	ND	0.16	0.06
Mn	ND	0.09	0.04
Cr	ND	0.09	0.06
Ni	ND	0.07	0.05
Cs	ND	0.02	0.02
Zr	ND	0.01	0.01
B	ND	ND	ND
Al	ND	ND	ND
Ti	ND	ND	ND
Nb	ND	ND	ND
Si	ND	ND	ND
Ca	ND	ND	ND
Fe	ND	ND	ND
Cd	ND	ND	ND
Sb	ND	ND	ND
W	ND	ND	ND

[a] ND – not detected/below detectable limits.

The overall similarity between the simulated and NSB-derived effluents indicates that the prepared simulant provides a very good approximation of true waste conditions. As expected, high concentrations of Na and K from the waste solution (NaOH, KOH) were leached from NSB. Another source of Na is the Na^+ counterions from Na-polyacrylate, which were likely replaced by acidic protons to form polyacrylic acid. The presence of Cs, Zr, and stainless steel corrosion products may significantly affect the radiochemical purity of recycled Mo upon irradiation, if these impurities are not removed. The final mass of Mo recovered per gram of NSB gel was 2.3 mg (simulant) and 1.9 mg (RadioGenix). Judging from the RadioGenix waste recovery, 1.9 g of Mo can be recovered per-kg waste gel using this method.

3.5 SOLVENT EXTRACTION OF RECOVERED Mo

Large-scale liquid-liquid extraction of Mo in HCl has been previously developed by Argonne for the recycle of enriched Mo material and is discussed in the literature [12], [13]. In strong HCl solutions, Mo can be extracted quantitatively using 30% TBP in TCE. This process achieves good decontamination with respect to Na and K, both of which are present at g/L levels in solutions recovered from NSB. The NSB effluent contains ~5M HCl, 1.5M Na^+, 0.05M K^+, dissolved brilliant blue dye, and other organics. Table 5 shows Mo loss after solvent extraction of the NSB effluent. The data show that there is minimal direct interference from organic contaminants with the extraction of Mo by TBP (98% recovery).

TABLE 5 Mo losses (± S.D.) during solvent extraction of Mo from recovered NSB waste solution, acidified to 5M acid concentration using HCl.

	Volume (L)	Mo Lost (%)	Mo conc. (mM)
NSB effluent	0.820	-	19.5
Acidified solution	1.049	-	15.2
Stripped solution	1.049	2% ± 1%	14.8

The loss of a few percent of Mo is due to the formation of a solid third phase at the aqueous-organic interface after mixing. The thin interfacial film shown in Figure 9 appeared in all experiments where effluents from NSB extraction were used. It appears to be the result of the aggregation of amphiphilic organic molecules suspended in the aqueous solution. The film was easily removed by spatula in small-scale experiments. However, it would interfere with large-scale automated processing schemes where centrifugal contactors or mixer-settler-type extraction may be used.

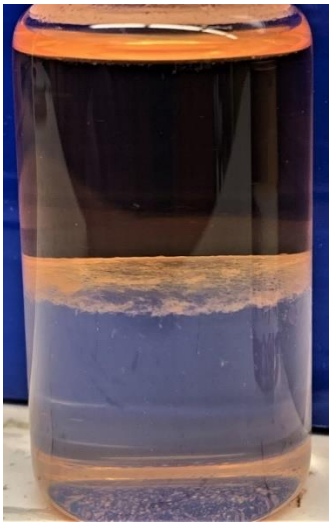

FIGURE 9 Contacting NSB effluent with 30% TBP in TCE resulted in third-phase formation at the aqueous-organic interface.

Numerous approaches to removing these organic contaminants were tried (e.g., filtration, centrifugation, pH-adjustment, solvent exchange, pre-contacted organic phase), but they were not able to adequately separate dissolved organics to prevent third-phase formation. Therefore, extraction chromatography using TBP resin was briefly investigated as an alternative to solvent extraction which may avoid the problems associated with third-phase formation. Additionally, the use of TBP resin could simplify the procedure to separate Mo from the remaining organic material, concentrate Mo on the column, and elute it into ammonium hydroxide solution.

The preliminary results from a 1-g TBP resin column are presented in Figure 10. The data suggest that the resin is highly effective at concentrating Mo from the complex feed matrix (NSB-derived) and eluting concentrated Mo. The sharp elution of Mo by NH_4OH suggests fast kinetics of MoO_2Cl_2 conversion to MoO_4^{2-}, which is consistent with the stripping behavior of Mo in solvent extraction. A separate column experiment confirmed this result and further suggested that the loading capacity of TBP resin for Mo in HCl is between 31 and 36 mg Mo/g TBP resin. However, fundamental studies will be needed to determine resin characteristics before designing a full-scale column.

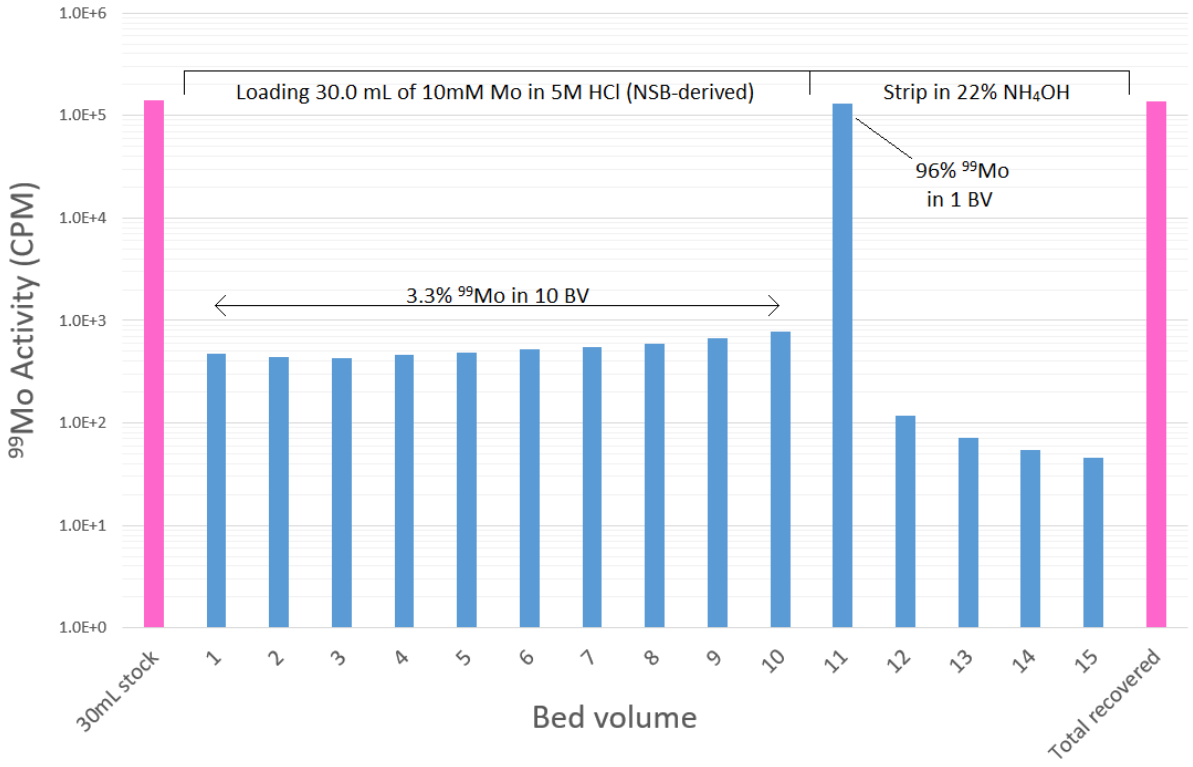

FIGURE 10 Loading and elution profiles from TBP resin (1.0 g resin) column chromatography of 10 mM Mo in 5 MHCl + 1.5M Na^+. Bed volume (BV) was approximately 3.0 mL.

The reason why a few percent of Mo was lost during the loading stage is unclear. One possible explanation is that unanchored TBP molecules are washing out through the column with the liquid phase. This problem could be corrected with more thorough washing of the resin before loading. But the determination of optimal feed conditions such as HCl concentration, flow rate, and weight distribution values were not in the scope of this report and will be presented in a separate work.

Mo was loaded onto the TBP column and directly eluted into NH_4OH. The product was evaporated and washed with 100% ethanol to produce a crystalline Mo product that was verified by X-ray diffraction. Evaporation of Mo in excess NH_4OH will produce the AHM product, which is insoluble in ethanol. Alternatively, the loaded column may be washed with HCl to

remove adsorbed organics and then eluted to produce a clear NH_4OH product. Quantitative analysis and optimization of these steps will be necessary to obtain the AHM product with the desired purity and yield.

4 CONCLUSION

The chemical flow sheet in Figure 11 depicts the proposed Mo recycle process and recovery yields. The proposed process results in very high Mo recoveries from solidified RadioGenix waste, in a chemical form that is readily recycled into new targets. The extraction of Mo from NSB can be achieved by contacting the gel with strong HCl solutions. A strong acidic environment collapses the hydrogel, which densifies into a solid phase and releases the absorbed solution. Using HCl prevents molybdenyl coprecipitation with the polymer, owing to formation of neutral chloro-complexes that are freely released to the liquid phase. Near-quantitative Mo recoveries can be obtained after two HCl contacts (deswelling + soak). The solid waste mass of precipitated NSB constitutes 75% of the initial RadioGenix mass and can be subsequently air-dried to produce a low-activity, compact waste form.

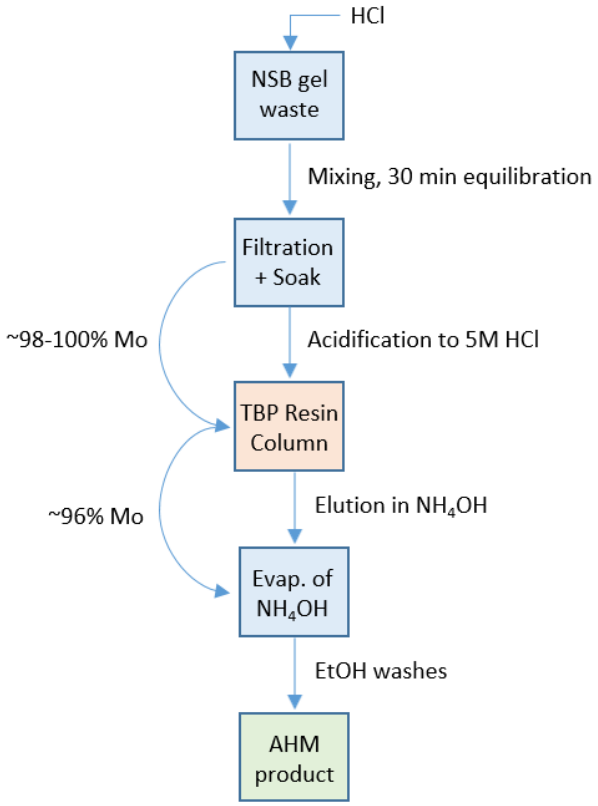

FIGURE 11 Proposed flow chart for the recovery of Mo from NSB, with stepwise recovery yields

The use of high concentrations of HCl with NSB polymer resulted in the leaching out of small amounts of organic impurities. This leaching may be due to amide hydrolysis of crosslinker groups, or to chain scission. Organic molecules with surfactant properties then accumulate in the liquid phase and cause the formation of an interfacial third phase during solvent extraction. Various techniques were tested to separate the dispersed organic material from recovered solutions, including activated charcoal chromatography, nanofiltration, centrifugation, pH-controlled precipitation, Ca^{2+} precipitation, and pre-contacting with an organic phase. However, these techniques were not sufficient to avoid the formation of a third phase, which prevents the use of large-scale solvent extraction methods.

Preliminary experiments using extraction chromatography with TBP resin showed promising progress toward resolving the problems associated with the third phase. Mo was adsorbed on the resin and eluted (96%) in a very low volume of NH_4OH. Mo can then be crystallized as AHM and washed with ethanol to remove remaining organic material.

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